

## ISOMERISM

# The same but different

Electromerism is an unfamiliar concept to many chemists and refers to molecules that are not conventional isomers but instead differ in how the electrons are distributed across their structure. A novel example of such electromers has now been demonstrated.

Thomas Bally

Isomerism is a central concept in chemistry and all who study this branch of science learn that molecules of the same elemental composition may differ in the way their constituent atoms are connected by chemical bonds (constitutional isomers) or in the spatial arrangement of the chemical bonds (stereoisomers). The latter class can also be subdivided to distinguish diastereomers (for example, *cis-trans*- or *E-Z*-isomers, conformers or rotamers) from molecules that are mirror images of each other (enantiomers).

Another, less familiar class of isomers are 'electro-isomers' (known also by their short name, electromers). These are pairs of molecules that do not differ in their constitution, nor much in the spatial disposition of the bonds between the atoms, but solely in the way the electrons are distributed amongst the atoms and the bonds that link them.

The most obvious class of electromers are excited electronic states, but as those have usually only a very fleeting existence, they cannot be put on an equal footing with different stable ground-state structures. In principle, states of different multiplicity such as those that occur in spin crossover compounds for example, may be regarded as electromers, but in that research field the term 'spin isomerism' is used to describe such species.

Electromers of the same multiplicity are most often encountered in transition metal complexes carrying ligands that can exist in different oxidation states, such as the phenoxy/phenolate or the quinone/semiquinone/catechol groups<sup>1</sup>. In some such cases, equilibria between distinct electromers of the form  $M^z(L_n^y) \rightleftharpoons M^{z-e}(L_n^{z+e})$  (where  $z$ ,  $y$  and  $e$  refer to charges) can be observed to shift on photolysis, or on changing external parameters such as temperature or pressure (if  $e > 1$ , the  $e$  electrons may be transferred to  $n$  different ligand molecules). Unfortunately, such electromers have recently been named 'valence tautomers'<sup>1</sup>, which can lead to some confusion because in organic chemistry the term 'tautomer' is reserved for isomers that differ in their bonding pattern to hydrogen.

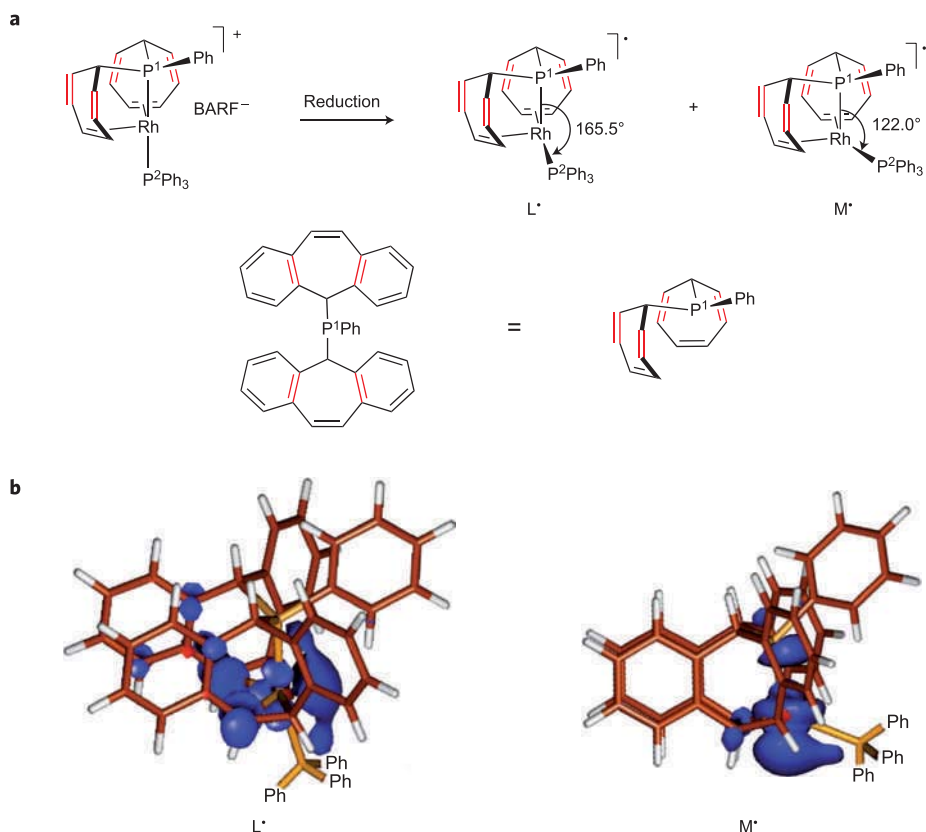
There are, however, some cases where electromerism is of a more subtle nature. Now writing in *Angewandte Chemie International Edition*, Grützmacher, de Bruin and colleagues present an intriguing organometallic case in which the electromers do not require redox-active ligands<sup>2</sup>.

They studied a rhodium complex carrying *bis*(dibenzotriptyl)phosphine (where the phosphorous atom is denoted P<sup>1</sup>) and triphenylphosphine (P<sup>2</sup>) ligands with the arrangement shown in Fig. 1a. The complex was first prepared in its

cationic form, which is stable if paired with the very non-nucleophilic B[3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>4</sub><sup>-</sup> ('BARF') anion. On one-electron reduction using elemental sodium, sodium naphthalenide or CoCp\*<sub>2</sub> (Cp\* = pentamethylcyclopentadienyl), two distinct radicals were formed that Grützmacher, de Bruin and co-workers named L<sup>•</sup> and M<sup>•</sup>. The two species were fully characterized by different forms of electron paramagnetic resonance (EPR) spectroscopy, and the L<sup>•</sup>  $\rightleftharpoons$  M<sup>•</sup> equilibrium could be reversibly shifted from 66% of L<sup>•</sup> at 340 K to 88% of L<sup>•</sup> at 190 K.

To understand the structure of the radicals, density functional theory (DFT) calculations were carried out that revealed two distinct potential energy minima within approximately 2 kcal mol<sup>-1</sup>, L<sup>•</sup><sub>calc</sub> and M<sup>•</sup><sub>calc</sub> (in addition to a third one, L<sup>•</sup>'<sub>calc</sub>, which, however, differs from L<sup>•</sup><sub>calc</sub> only by rotation around the Rh-P<sup>2</sup>Ph<sub>3</sub> bond). Apart from the Rh-P<sup>2</sup>Ph<sub>3</sub> bond length which is 0.047 Å longer in L<sup>•</sup><sub>calc</sub> the two isomers have very similar bond lengths, but M<sup>•</sup><sub>calc</sub> distinguishes itself by having a much smaller P<sup>1</sup>-Rh-P<sup>2</sup> angle, which gives it a structure similar to a trigonal bipyramidal complex such as is observed when the P<sup>1</sup>Ph moiety is replaced by the more electron-donating SiMe group (Fig. 1a).

The differences in the electronic structure of L<sup>•</sup> and M<sup>•</sup> express themselves most clearly



**Figure 1** | Electromerism in an organometallic compound. **a.** Formation and structures of radicals  $L^*$  and  $M^*$ . The benzo rings that are annellated to the tropylium ligands are omitted for clarity and replaced with red double bonds. **b.** The different spin densities (shown in blue) of the electromeric radicals  $L^*$  and  $M^*$ . Part b reproduced with permission from ref. 2, © Wiley 2010.

in their EPR spectra, especially the difference in the hyperfine coupling constants to the  $^{31}\text{P}$  atom in Fig. 1a ( $A_{\text{iso}} = 53$  MHz for  $L^*$  versus 602 MHz for  $M^*$ ) and, to a lesser degree, in that to the  $^{103}\text{Rh}$  atom ( $A_{\text{iso}} = 10$  MHz for  $L^*$  versus 3 MHz for  $M^*$ ). The DFT calculations show, however, that the changes in  $A_{\text{iso}}$  do not translate directly into changes in spin density on these atoms, presumably due to the changes in hybridization at the rhodium atom: although the calculated spin density on the  $\text{P}^1$  atom increases from 12% to 28% on going from  $L^*$  to  $M^*$ , so does that on rhodium (from 33 to 58%).

More importantly, spin density shifts from the hydrocarbon parts of the ligands — which carry 46% of the spin in  $L^*$  — to the central  $\text{P}^1$ –Rh– $\text{P}^2$  moiety, which carries nearly 90% of the spin in  $M^*$  (with more

than half of that on the rhodium atom) — see Fig. 1b. This leads Grützmacher, de Bruin and co-workers to describe  $L^*$  as a “strongly delocalized organometallic radical” whereas they consider  $M^*$  as a “metallo radical with a high localization of spin in the Rh– $\text{P}^1$  bond”.

In a molecular orbital (MO) picture, the odd electron in  $L^*$  occupies an MO that is localized mostly on the two  $\text{P}^1$ -(dibenzotropylium) ligands, whereas in  $M^*$  it resides in an MO that is localized mostly on the Rh- and the  $\text{P}^1$ -atom. With this perspective,  $M^*$  can be regarded as a low-lying excited state of  $L^*$  that gains a spectroscopically palpable existence by virtue of a barrier (calculated as approximately 3 kcal mol $^{-1}$ ) that separates it from its ‘electronic isomer’  $L^*$ .

As electronic reorganizations are inherently barrierless, the barrier that separates  $M^*$  from  $L^*$  must arise because the ground state of  $M^*$  correlates with an excited state of  $L^*$  along the deformation that leads from the structure of  $M^*$  to the structure of  $L^*$ , and *vice versa*. Indeed, it would be interesting to know where the electronic state of  $L^*$ , which corresponds to the electronic structure of  $M^*$ , lies and *vice versa*, but Grützmacher, de Bruin and co-workers do not give any information on that. The rhodium complex described does, however, demonstrate that electromerism in organometallic chemistry is not restricted to complexes carrying redox-active ligands. It can occur in cases where an unpaired electron occupies one or another orbital of a complex, provided that there is a suitable distortion that stabilizes the ‘excited state’ to the extent that it becomes an isomeric ground state.

This situation is reminiscent of the one that prevails in the open-shell compounds that are subjected to Jahn–Teller distortion, except that in those cases, only one of the ‘electromers’ usually corresponds to a potential energy minimum, whereas the other is a transition state for its automerization<sup>3</sup>. In recent research<sup>4</sup> we have observed a case of true electromerism in a pair of organic radical cations containing two allylic moieties. The two electromers distinguish themselves by the nature of the singly occupied MO (SOMO), which in one case corresponds to the positive, and in the other to the negative combination of the constituent allylic SOMOs. This example shows that the phenomenon of electromerism is not bound to the presence of transition metals — and, as Grützmacher, de Bruin and co-workers have shown, to redox-active ligands — and thus it may be more prevalent throughout chemistry than we might think.

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